

### **WHAT IS CLAIMED IS:**

1. A microarray comprising:  
a diazotized tether group bound to a substrate; and  
at least one polypeptide covalently bound to said diazotized tether group.
2. The microarray of claim 1, wherein said polypeptide includes at least one terminal histidine residue.
3. The microarray of claim 2, wherein said polypeptide is covalently bound to said diazotized tether group at said at least one terminal histidine residue.
4. The microarray of claim 2, wherein said polypeptide includes a terminal series of 6 histidine residues.
5. The microarray of claim 4, wherein said polypeptide is covalently bound to said diazotized tether group at one of said histidine residues.
6. The microarray of claim 2, wherein said polypeptide includes a terminal series of up to 20 histidine residues.
7. The microarray of claim 6, wherein said polypeptide is covalently bound to said diazotized tether group at one of said histidine residues.
8. The microarray of claim 1, wherein said polypeptide is bound to said diazotized tether group by an internal histidine residue of said polypeptide.
9. The microarray of claim 1, wherein said polypeptide includes at least one terminal tyrosine residue.
10. The microarray of claim 9, wherein said polypeptide is covalently bound to said diazotized tether group at said terminal tyrosine residue.

11. The microarray of claim 9, wherein said polypeptide includes a terminal series of 6 tyrosine residues.
12. The microarray of claim 11, wherein said polypeptide is covalently bound to said diazotized tether group at one of said tyrosine residues.
13. The microarray of claim 9, wherein said polypeptide includes a terminal series of up to 20 tyrosine residues.
14. The microarray of claim 13, wherein said polypeptide is covalently bound to said diazotized tether group at one of said tyrosine residues.
15. The microarray of claim 1, wherein said polypeptide is bound to said diazotized tether group by an internal tyrosine residue of said polypeptide.
16. The microarray of claim 1, wherein said substrate comprises a glass substrate.
17. The microarray of claim 16, wherein said substrate comprises a glass bead.
18. The microarray of claim 14, wherein said substrate comprises a glass slide.
19. The microarray of claim 1, wherein said substrate comprises a polymer substrate.
20. The microarray of claim 19, wherein said substrate comprises a plastic substrate.
21. The microarray of claim 20, wherein said substrate comprises polyethylene terephthalate.
22. The microarray of claim 1, wherein said substrate comprises a silicon wafer.
23. The microarray of claim 1, wherein said substrate comprises a ceramic substrate.
24. The microarray of claim 1, wherein said substrate comprises a metal oxide substrate.

25. The microarray of claim 1, wherein said substrate comprises a clay substrate.
26. The microarray of claim 1, wherein said substrate comprises a noble metal substrate.
27. The microarray of claim 26, wherein said substrate comprises a gold substrate.
28. The microarray of claim 26, wherein said substrate comprises a silver substrate.
29. The microarray of claim 26, wherein said substrate comprises a copper substrate.
30. The microarray of claim 1, wherein said at least one polypeptide comprises a plurality of polypeptides.
31. The microarray of claim 30, wherein said plurality of polypeptides comprises at least two different polypeptides.
32. The microarray of claim 1, wherein said polypeptide comprises a protein.
33. The microarray of claim 1, wherein said substrate has a thickness of approximately 1 mm.
34. The microarray of claim 1, wherein said diazotized tether group comprises a siloxy diazonium group.
35. The microarray of claim 34, wherein said siloxy diazonium group comprises p-diazoniumphenyltrimethoxysilane salt.
36. The microarray of claim 1, wherein said diazotized tether group comprises a thiolate diazonium group.
37. The microarray of claim 34, wherein said thiolate diazonium group comprises p-diazoniumthiophenol salt.

38. A method for forming a microarray comprising:

(a) treating an oxidized surface of a substrate with a siloxy amine to form a siloxy amine treated substrate;

(b) treating said siloxy amine treated substrate with a diazotizing agent to form a siloxy diazotized substrate; and

(c) contacting said siloxy diazotized substrate with at least one polypeptide to form said microarray in which said at least one polypeptide is covalently bound to said siloxy diazotized substrate.

39. The method of claim 38, wherein said polypeptide includes at least one terminal histidine residue.

40. The method of claim 39, wherein said polypeptide is covalently bound to said siloxy diazotized substrate at said at least one terminal histidine residue.

41. The method of claim 38, wherein said polypeptide includes a terminal series of 6 histidine residues.

42. The method of claim 41, wherein said polypeptide is covalently bound to said siloxy diazotized substrate at one of said histidine residues.

43. The method of claim 39, wherein said polypeptide includes a terminal series of up to 20 histidine residues.

44. The method of claim 43, wherein said polypeptide is covalently bound to said siloxy diazotized substrate at one of said histidine residues.

45. The method of claim 38, wherein said polypeptide is bound to said siloxy diazotized tether group by an internal histidine residue of said polypeptide.

46. The method of claim 38, wherein said polypeptide includes at least one terminal tyrosine residue.

47. The method of claim 46, wherein said polypeptide is covalently bound to said siloxy diazotized substrate at said terminal tyrosine residue.
48. The method of claim 46, wherein said polypeptide includes a terminal series of 6 tyrosine residues.
49. The method of claim 48, wherein said polypeptide is covalently bound to said siloxy diazotized substrate at one of said tyrosine residues.
50. The method of claim 46, wherein said polypeptide includes a terminal series of up to 20 tyrosine residues.
51. The method of claim 50, wherein said polypeptide is covalently bound to said siloxy diazotized substrate at one of said tyrosine residues.
52. The method of claim 38, wherein said polypeptide is bound to said siloxy diazotized tether group by an internal tyrosine residue of said polypeptide.
53. The method of claim 38, wherein said siloxy amine comprises p-aminophenyl trimethoxysilane (ATMS).
54. The method of claim 38, wherein said diazotizing agent comprises  $\text{NaNO}_2$  and  $\text{HCl}$ .
55. The method of claim 38, wherein said siloxy diazotized substrate is formed from said siloxy amine treated substrate by exposing said siloxy amine treated substrate with  $\text{NaNO}_2$  and at  $0-25^\circ\text{C}$  for 10-30 minutes.
56. The method of claim 38, wherein said siloxy diazotized substrate is formed from said siloxy amine treated substrate by exposing said siloxy amine treated substrate with  $\text{NaNO}_2$  and  $\text{HCl}$  at  $0-4^\circ\text{C}$  for 30 minutes.

57. The method of claim 38, further comprising treating a substrate surface with an oxidizing agent to form said oxidized surface.
58. The method of claim 57, wherein said substrate comprises a polymer substrate.
59. The method of claim 58, wherein said substrate comprises a plastic substrate.
60. The method of claim 59, wherein said substrate comprises polyethylene terephthalate.
61. The method of claim 38, wherein said siloxy diazotized substrate comprises a glass substrate.
62. The method of claim 61, wherein said siloxy diazotized substrate comprises a glass bead.
62. The method of claim 61, wherein said siloxy diazotized substrate comprises a glass slide.
63. The method of claim 38, wherein said siloxy diazotized substrate comprises a polymer substrate.
64. The method of claim 63, wherein said siloxy diazotized substrate comprises a plastic substrate.
65. The method of claim 64, wherein said siloxy diazotized substrate comprises polyethylene terephthalate.
66. The method of claim 38, wherein said siloxy diazotized substrate comprises a silicon wafer.
67. The method of claim 38, wherein said siloxy diazotized substrate comprises a ceramic substrate.

68. The method of claim 38, wherein said siloxy diazotized substrate comprises a clay substrate.
69. The method of claim 38, wherein said siloxy diazotized substrate comprises a p-diazoniumphenyltrimethoxysilane salt bound to said substrate.
70. The method of claim 38, wherein said at least one polypeptide comprises a plurality of polypeptides.
71. The method of claim 70, wherein said plurality of polypeptides comprises at least two different polypeptides.
72. The method of claim 38, wherein said polypeptide comprises a protein.
73. The method of claim 38, wherein said substrate has a thickness of approximately 1 mm.
74. The method of claim 38, further comprising repeating step (c) one or more times and removing free polypeptides from said microarray after every time step (c) is performed without removing bound polypeptides from said microarray.
75. The method of claim 74, wherein each time step (c) is performed a different polypeptide is bound to said substrate.
76. A method for forming a microarray comprising:  
treating a noble metal substrate with a thiolate amine to form a thiolate amine treated substrate;  
treating said thiolate amine treated substrate with a diazotizing agent to form a thiolate diazotized substrate; and  
contacting said thiolate diazotized substrate with at least one polypeptide to form said microarray in which said at least one polypeptide is covalently bound to said thiolate diazotized substrate.

77. The method of claim 76, wherein said polypeptide includes at least one terminal histidine residue.

78. The method of claim 77, wherein said polypeptide is covalently bound to said thiolate diazotized substrate at said at least one terminal histidine residue.

79. The method of claim 77, wherein said polypeptide includes a terminal series of 6 histidine residues.

80. The method of claim 79, wherein said polypeptide is covalently bound to said thiolate diazotized substrate at one of said histidine residues.

81. The method of claim 77, wherein said polypeptide includes a terminal series of up to 20 histidine residues.

82. The method of claim 81, wherein said polypeptide is covalently bound to said thiolate diazotized substrate at one of said histidine residues.

83. The method of claim 76, wherein said polypeptide is bound to said thiolate diazotized tether group by an internal histidine residue of said polypeptide.

84. The method of claim 76, wherein said polypeptide includes at least one terminal tyrosine residue.

85. The method of claim 84, wherein said polypeptide is covalently bound to said thiolate diazotized substrate at said terminal tyrosine residue.

86. The method of claim 84, wherein said polypeptide includes a terminal series of 6 tyrosine residues.

87. The method of claim 86, wherein said polypeptide is covalently bound to said thiolate diazotized substrate at one of said tyrosine residues.



88. The method of claim 84, wherein said polypeptide includes a terminal series of up to 20 tyrosine residues.
89. The method of claim 88, wherein said polypeptide is covalently bound to said thiolate diazotized substrate at one of said tyrosine residues.
90. The method of claim 76, wherein said polypeptide is bound to said thiolate diazotized tether group by an internal tyrosine residue of said polypeptide.
91. The method of claim 76, wherein said thiolate amine comprises 4-aminothiophenol.
92. The method of claim 76, wherein said diazotizing agent comprises  $\text{NaNO}_2$  and  $\text{HCl}$ .
93. The method of claim 76, wherein said thiolate diazotized substrate is formed from said thiolate amine treated substrate by exposing said thiolate amine treated substrate with  $\text{NaNO}_2$  and  $\text{HCl}$  at 0-25°C for 10-30 minutes.
94. The method of claim 76, wherein said thiolate diazotized substrate is formed from said thiolate amine treated substrate by exposing said thiolate amine treated substrate with  $\text{NaNO}_2$  and  $\text{HCl}$  at 0-4°C for 30 minutes.
95. The method of claim 76, wherein said thiolate diazotized substrate comprises a gold metal substrate.
96. The method of claim 76, wherein said thiolate diazotized substrate comprises a silver metal substrate.
97. The method of claim 76, wherein said thiolate diazotized substrate comprises a copper substrate.
98. The method of claim 76, wherein said thiolate diazonium substrate comprises a p-diazoniumthiophenol salt bound to said substrate.

99. The method of claim 76, wherein said at least one polypeptide comprises a plurality of polypeptides.

100. The method of claim 99, wherein said plurality of polypeptides comprises at least two different polypeptides.

101. The method of claim 76, wherein said polypeptide comprises a protein.

102. The method of claim 76, wherein said thiolate diazotized substrate has a thickness of approximately 1 mm.